

The effect of temperature on the kinetics of diacrylate photopolymerizations studied by Real-time FTIR spectroscopy

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Dedicated to Prof. Reiner Mehnert on the occasion of his 60th birthday

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Abstract

Real-time FTIR spectroscopy was used to study the effect of temperature on the kinetics of photopolymerization from room temperature up to 160°C. A highly viscous epoxy diacrylate and tripropylene glycol diacrylate (TPGDA) as systems of lower viscosity were used to study the influence of viscosity on the polymerization rate, the induction period, and the ultimate conversion. Different behaviour was observed at temperatures below and above ca. 90°C. In the epoxy diacrylate, the polymerization rate first distinctly increases with temperature due to the drop of viscosity, whereas in TPGDA the polymerization rate only little increases or is even independent of temperature depending on the photoinitiator used. The induction period decreases due to the decreasing solubility of oxygen in the reactive formulation. At higher temperatures, termination processes lead to a decrease of the polymerization rate if morpholino ketones are used for initiation. Simultaneously, the induction period re-increases. In contrast, systems initiated by a hydroxy alkylphenone or benzildimethyl ketal continue the trends from below 90°C. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Real-time FTIR spectroscopy; Photopolymerization; Effect of temperature

1. Introduction

Radiation curing has become a well-accepted technology, which has found a large number of industrial applications mainly in the coating and printing sector, in the manufacture of adhesives, and in microelectronics. It allows the rapid transformation of liquid multifunctional monomers and oligomers into solid polymer coatings simply by exposure to UV radiation in the presence of a photoinitiator.

In many applications, the maximum cure speed, which can be achieved, is one of the key parameters for the efficiency of the process. The maximum cure speed depends on both the induction period t_i during which the inhibiting effect of oxygen has to be overcome and the conversion time t_{con} which is determined by the polymerization rate R_p of the formulation. Both t_i and t_{con} are typically in the range of some milliseconds. For increasing the cure speed, the induction period has to be shortened and the maximum polymerization rate must be increased as much as possible. Therefore, the effect of all parameters, which help to attain

this objective, is of fundamental interest. In this study, the influence of temperature on R_p and t_i will be studied.

One of the advantages of UV curing technology is that it can be carried out at ambient temperature. However, in practice the curing reactions are often performed at increased temperatures. Usually, this is inevitable due to the heating of the layer by the infrared part of the lamp emission or by the release of the reaction enthalpy of thicker coatings. On the contrary, a higher temperature may be necessary to reduce the viscosity of the formulation to enable its application to the substrate or to increase the degree of cure to improve the final properties of the product, for example to avoid migration of residual monomers or accelerated ageing due to unconverted reactive functionalities.

However, an increase of temperature will also have a marked effect on the kinetics of photopolymerization reactions. Propagation and termination may be sensitive to diffusional effects associated with the gel point or the glass transition. The propagation reaction strongly depends on the segmental mobility of the reactive chain ends, whereas the termination reaction is affected by the reduced mobility of the radical sites bound to the developing network [1–3]. At low conversion, this leads to autoacceleration [4]. When

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the diffusion of the monomer becomes hindered at higher conversion, deceleration occurs [1,5]. Moreover, pendent double bonds may show different reactivity as compared to those bound to free monomer molecules [5]. If the glass transition temperature of the reacting system approaches the curing temperature, segmental mobility and thus propagation is severely restricted. Radicals can become trapped in inaccessible positions [2,5,6]. After vitrification, reaction may cease leaving the remaining functional groups unreacted.

It is obvious, that all those processes should be influenced by temperature variations due to their strong dependence on diffusional effects. Further, the termination mechanism may change with temperature since chain transfer is favoured by higher temperatures [4]. Consequently, a distinct dependence of the polymerization kinetics on temperature is expected which must be determined experimentally.

Photo-DSC is by far the most widely used technique to follow the kinetics of photoinitiated polymerization reactions [7]. However, photo-DSC suffers from a rather long response time of the calorimeter device (about 1.5 s [1]) and a low thermal conductivity of most of the samples that strongly limit its time resolution. This makes it impossible to monitor reactions which occur within less than 1 min [8] thus requiring irradiation with very low intensities and/or a considerable reduction of the amount of photoinitiator added. Nevertheless, photo-DSC has been extensively used in the past to monitor photoinitiated-curing reactions. In particular, several investigations have been performed in order to study the effect of temperature on the kinetics of the photopolymerization of acrylates and methacrylates [1,9–17], epoxides [18], vinyl ethers [19] and thiol–ene systems [20].

Whereas the maximum rate of polymerization can be obtained from DSC measurements if appropriate experimental conditions have been chosen it is quite difficult to study the behaviour of the induction period by this method due to the restrictions with respect to the response time. Real-time FTIR (RTIR) spectroscopy does not suffer from such limitations. It is the only analytical method which offers the necessary time resolution (in the range of some milliseconds) and the analytic capabilities for monitoring and analyzing of photoinitiated reactions proceeding under experimental conditions which are as close as possible to those in technical applications. In particular, it allows a quantitative determination of the conversion of specific reactive functional groups such as acrylates and epoxides. RTIR spectroscopy has been successfully used to investigate the kinetics of photopolymerization reactions in dependence on various experimental parameters [21–25], the reactivity of monomers and oligomers [26,27], and the performance of photoinitiator systems [28–31]. However, only very few studies have been reported wherein the potential of RTIR spectroscopy was used to examine the effect of temperature on the kinetics of the photopolymerization [32,33].

The present paper describes a series of experiments by real-time FTIR-ATR spectroscopy during which various kinetic parameters such as R_p , t_i and the residual unsaturation were determined in dependence on temperature between 25 and 160°C. In addition, the effect of the viscosity of the acrylate was investigated. Since the viscosity of acrylate oligomers strongly depends on temperature, a distinct effect of viscosity on the kinetics is expected too. Moreover, the influence of the photoinitiator selected for initiation was considered. In all experiments, monochromatic UV light was used for irradiation in order to avoid heating of the samples from the infrared emission of the mercury arc lamp.

2. Experimental

2.1. Real-time FTIR-ATR spectroscopy

Real-time FTIR Spectroscopy (RTIR) with Attenuated Total Reflection (ATR) was used to study the kinetics of photopolymerization reactions. Spectra were recorded using a Biorad FTS 6000 spectrometer and a Golden Gate single reflection diamond ATR unit (Graseby Specac) which can be heated up to 200°C. The spectrometer reaches a temporal resolution of 11 ms at a spectral resolution of 16 cm^{-1} .

UV-irradiation was performed with an Osram HBO 100 W mercury arc lamp which is equipped with a water filter for blocking infrared radiation and a 313 nm metal interference filter (Andover) to provide monochromatic light. The UV radiation is focused on the surface of the diamond ($2 \times 2 \text{ mm}^2$). Its intensity at the sample position was measured by a radiometer with a SiC detector which is calibrated to radiation with a wavelength of 313 nm by chemical actinometry [34]. An electronic shutter (Vincent) controlled by the spectrometer computer enables exact synchronization between UV exposure and IR spectra recording.

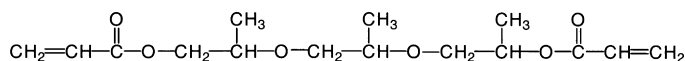
The sample on the diamond is covered by a quartz plate. The thickness of the sample is set by a circular depression in this plate with a depth of 4 μm which was made by ion beam etching. Samples were irradiated in air. However, due to the quartz plate, only the oxygen dissolved in the mixture is relevant for inhibition.

A detailed description of the experimental setup is given in Ref. [24].

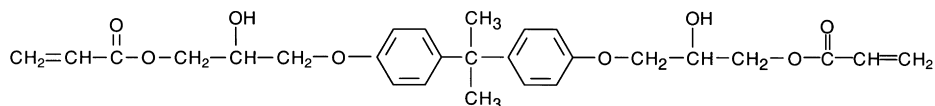
The kinetic conversion profiles were calculated from the decay of the absorption bands of the $\text{CH}=\text{CH}_2$ twisting vibration at 810 cm^{-1} (TPGDA) or the $\text{CH}=\text{CH}_2$ deformation mode at 1410 cm^{-1} (epoxy diacrylate) [35] by integration of the peak areas. The conversion vs. time curves and the kinetic data derived from them are averages from 10 to 20 measurements for each temperature.

2.2. Viscosimetry

Viscosities in the range between 10 and 15 000 mPa s



TPGDA



Bisphenol A Epoxy Diacrylate

Scheme 1.

(epoxy diacrylate) were determined using a coaxial cylinder viscosimeter (Haake Viscotester VT 500). The viscosities of TPGDA were measured by a Höppler viscosimeter.

2.3. Thermal analysis

Complementary thermal measurements were performed by differential scanning calorimetry (DSC) and thermogravimetry (TGA) using a Perkin Elmer DSC-7 and a thermogravimetric analyzer TGA-7. Every sample was scanned at least twice.

2.4. Samples

Tripolyene glycol diacrylate (TPGDA) and a bisphenol A epoxy diacrylate oligomer (BA-EpAc) with a molecular weight of 500 g mol^{-1} which is diluted with 25 wt.% TPGDA (EB 605 from UCB) were studied as acrylates with different viscosities (see Scheme 1).

As photoinitiators, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (BDMB; Irgacure IC 369), 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (TPMK; IC 907), 2,2-dimethoxy-1,2-diphenylethan-1-one (BDK; IC 651) and 2-hydroxy-2-methyl-1-phenyl-propanone (HAP; Darocur DC 1173; all from Ciba) were used. Their molar extinction coefficients at 313 nm are given in Table 1 [31] and the structures are plotted in Scheme 2.

After addition of the photoinitiator, the samples were treated in a sonication bath for 10 min to ensure that the photoinitiator is completely dissolved.

Table 1
Molar extinction coefficients of the photoinitiators at 313 nm [31]

Photoinitiator	Trade name	$\epsilon_{313 \text{ nm}}$ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)
HAP	DC 1173	90
BDK	IC 651	194
BDMB	IC 369	17 000
TPMK	IC 907	16 000

3. Results and discussion

3.1. Effect of temperature on the photopolymerization of a highly viscous oligomer

Epoxy acrylates are the most widely used group of radiation-curable oligomers. They are highly reactive and usually give hard, glossy and chemically resistant coatings. However, most epoxy acrylates are highly viscous products. Therefore, they have to be diluted with monomers such as TPGDA. EB 605 consists of an epoxy diacrylate which already contains 25 wt.% TPGDA resulting in a viscosity of 7500 mPa s at 25°C . In this investigation, it is used to study the effect of temperature on the kinetics of UV-initiated polymerization of a highly viscous acrylate.

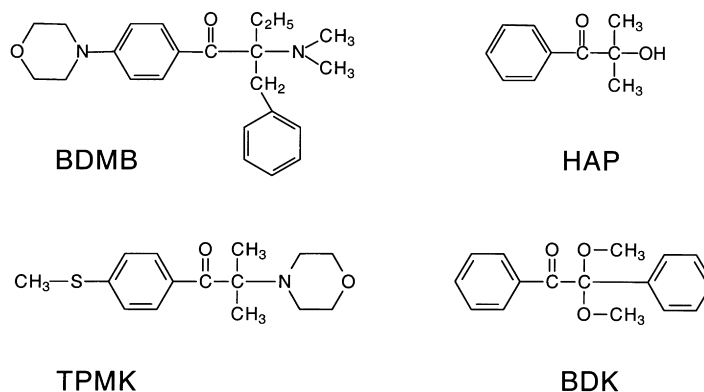
For initiation, 1 wt.% BDMB was added which is known to be one of the most effective photoinitiators at 313 nm [31]. Photopolymerization was performed by irradiation with an irradiance of 56 mW cm^{-2} at various temperatures in the range from 25 up to 160°C . Simultaneously, infrared spectra were recorded at a rate of 95 spectra per second. The decay of the double bond absorption in the epoxy diacrylate is shown in Fig. 1.

The most striking feature in Fig. 1 is the strong increase of the conversion when the temperature rises. The conversion of double bonds after continuous UV irradiation for 10 s is plotted in Fig. 2. A steady increase of the final conversion with increasing temperature is observed even when the temperature during exposure passes through the ultimate glass transition temperature of the epoxy diacrylate. The glass transition temperature of BA-EpAc cross-linked by electron beam curing (100 kGy) was found to be 84°C .

From the conversion curves in Fig. 1, the polymerization rate R_p was calculated according to

$$R_p = -\frac{d[M]}{dt} \quad (1)$$

where $[M]$ is the monomer concentration. Results are shown in Fig. 3. Some polymerization profiles for temperatures higher than 100°C is omitted for clarity. It can be clearly



Scheme 2.

seen that the maximum polymerization rate $R_{p,max}$ strongly increases with temperature up to 85°C. When the temperature is further increased, $R_{p,max}$ slows down again. Similar observations were also made with epoxy acrylates [11] and methacrylates [11,12,15] using photo-DSC.

In Fig. 4, the temperature dependence of the maximum polymerization rate of BA-EpAc is given as Arrhenius plot. From the slope of this plot, an apparent activation energy E_A of the photopolymerization reaction for temperatures lower than 85°C can be calculated and a value of 13.5 kJ mol⁻¹ was obtained. This is in accordance with values reported for epoxy (meth)acrylates which range from 10 [11] to 15.5 kJ mol⁻¹ [15].

The strong increase of $R_{p,max}$ between 25 and 85°C is due to the dramatic drop of the viscosity of the resin in this temperature region which is shown in Fig. 5. The reduction of the viscosity leads to a strong increase of molecular diffusional mobility and thus reactivity.

3.2. Effect of viscosity

The viscosity of a highly viscous oligomer can also be reduced by dilution with a monomer of lower viscosity. In order to estimate the contribution of the viscosity drop to the

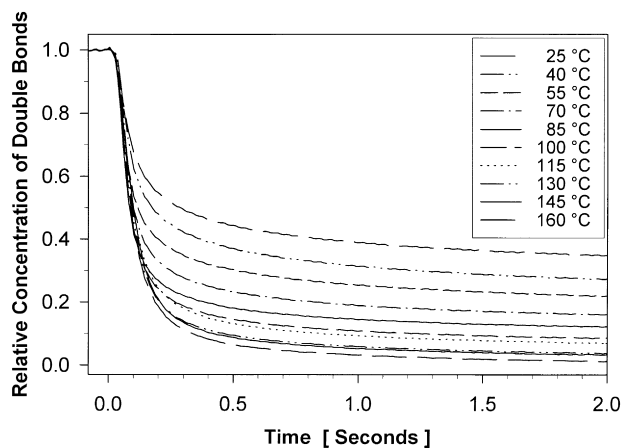


Fig. 1. Photopolymerization of BA-EpAc/1 wt.% BDMB at various temperatures (irradiance 56 mW cm⁻²).

temperature dependence of $R_{p,max}$, BA-EpAc was further diluted with TPGDA. The content of TPGDA in the mixture was varied between 25 (i.e. EB 605) and 65 wt.%. The viscosity reduction obtained this way is comparable to that of an increase of the temperature from 25 to 70°C (see Fig. 5).

The mixtures containing 1 wt.% BDMB were irradiated at ambient temperature under the same conditions like during the measurement of the temperature dependence of the epoxy diacrylate (Fig. 1). As expected, the conversion and the polymerization rate strongly increased with the decreasing viscosity of the formulation.

If $R_{p,max}$ of the mixtures is plotted together with the results of the temperature dependence of BA-EpAc (Fig. 4) vs. the initial viscosity each formulation, the data of both series fall perfectly on one line (Fig. 6a). However, the $R_{p,max}$ values of the two studies cannot be directly compared as the monomer concentration $[M]_0$ in the mixtures varied with the TPGDA content. Therefore, $R_{p,max}$ of both series was related to $[M]_0$. In Fig. 6b, this ratio is plotted in dependence on the initial viscosity.

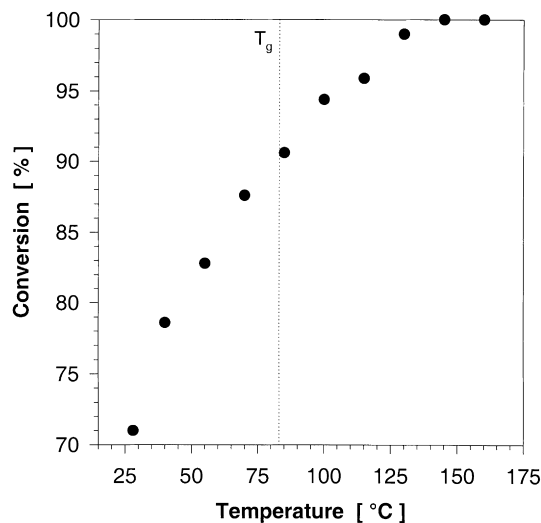


Fig. 2. Conversion of double bonds in BA-EpAc/1 wt.% BDMB after 10 s irradiation.

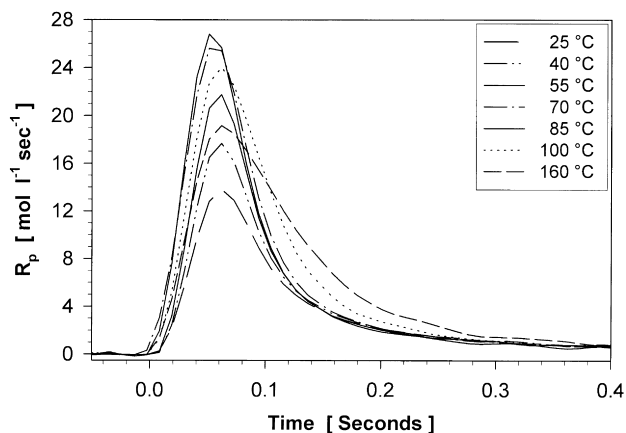


Fig. 3. Polymerization rate in BA-EpAc/1 wt.% BDMB.

The close correlation between both curves clearly demonstrates that the increase of the polymerization rate is largely due to the change of viscosity. However, the small difference between the two curves indicates an additional effect of temperature on the polymerization rate except of that due to viscosity reduction.

3.3. Effect of temperature on the photopolymerization of a low viscous diacrylate

3.3.1. Initiation with morpholino ketones

Whereas the viscosity of the epoxy diacrylate falls by more than two orders of magnitude when the temperature is increased from 25 to 85°C (Fig. 7), the viscosity of TPGDA, by contrast, is reduced in the same temperature range by less than one order of magnitude. Consequently, its maximum polymerization rate is expected to show a smaller increase than that of BA-EpAc.

The Arrhenius plot of TPGDA containing 0.1 wt.% BDMB is shown in Fig. 8. It is evident, that the maximum

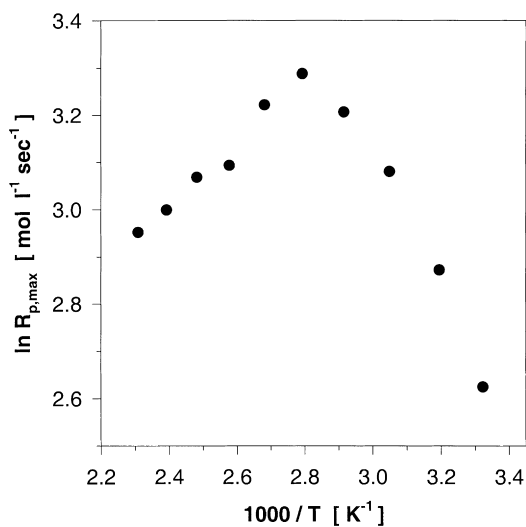


Fig. 4. Temperature dependence of the polymerization rate of BA-EpAc/1 wt.% BDMB.

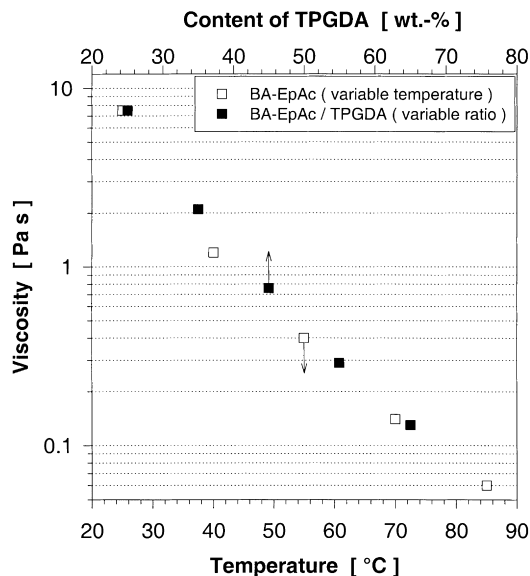


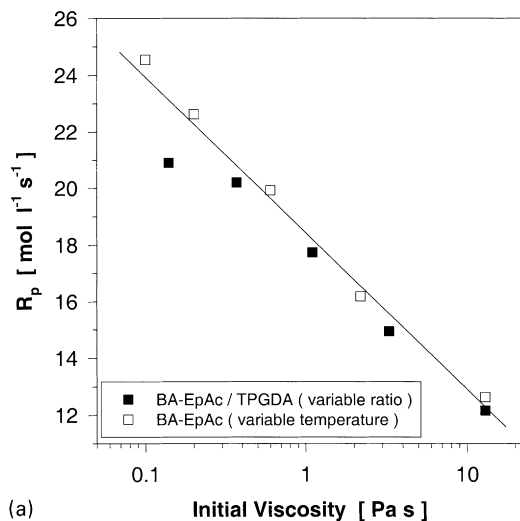
Fig. 5. Viscosity of BA-EpAc at various temperatures and of mixtures of BA-EpAc and TPGDA at various ratios.

polymerization rate does not change with temperature between 25 and 145°C. It neither shows the usual Arrhenius-like behaviour nor the drop of $R_{p,max}$ at about 90°C. This is an astonishing result for which the reason was not clear first. Therefore, the influence of the photoinitiator and its concentration was studied in more detail.

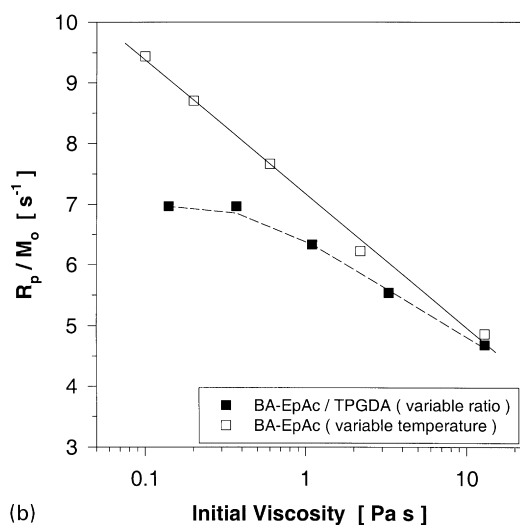
The concentration of the photoinitiator had been reduced as compared to the investigation of BA-EpAc in order to improve the adaptation of the reaction rate to the time resolution of RTIR spectroscopy (11 ms). As already mentioned above, BDMB is highly efficient at 313 nm. In order to check the effect of the photoinitiator, BDMB was replaced by another morpholino ketone (TPMK) which has also high performance at 313 nm. It was added to TPGDA at the same concentration. The temperature dependence of the kinetics of photopolymerization of this system was investigated under the same conditions like TPGDA/0.1 wt.% BDMB. Additionally, in a subsequent experiment the concentration of TPMK was increased to 1 wt.% in order to study the effect of initiator concentration. Both the Arrhenius plots are depicted in Fig. 9.

Comparing Figs. 8 and 9, it can be seen that the effect of temperature on the polymerization kinetics of TPGDA obviously shows a strong dependence on the photoinitiator used. Whereas $R_{p,max}$ is independent of the temperature in the whole temperature region studied if BDMB is used for initiation, this is the case only up to about 70°C with TPMK. At higher temperatures, a considerable drop of the maximum polymerization rate occurs.

In contrast to the selection of the photoinitiator, its concentration evidently does not play a significant role. The Arrhenius plots of TPGDA containing 0.1 or 1 wt.% TPMK show similar behaviour. Both the curves show the same gradual decay of $R_{p,max}$ starting at about 70°C.



(a)



(b)

Fig. 6. (a) Polymerization rate of BA-EpAc at various temperatures and of BA-EpAc/TPGDA mixtures at room temperature in dependence on the initial viscosity (photoinitiator: 1 wt.% BDMB, irradiance 56 mW cm^{-2}). (b) Normalized polymerization rate $R_p/[M]_0$ in dependence on the initial viscosity of BA-EpAc at various temperatures and of BA-EpAc/TPGDA mixtures at room temperature.

Another important kinetic parameter is the induction period t_i which may also be easily obtained from the RTIR measurements. Since the layers are covered by the quartz plate in the experimental setup used, the induction period is determined by the oxygen dissolved in the mixture only. The supply of atmospheric oxygen is completely suppressed by the quartz plate.

The temperature dependence of the induction period of TPGDA containing TPMK is plotted in Fig. 10. At first, t_i strongly decreases with the increasing temperature which is due to the decreasing solubility of oxygen in the acrylate [36] and the increasing diffusion rate in the reactive formulation. The decay is more pronounced in samples with lower photoinitiator content, because the lower concentration of radicals formed on irradiation a higher percentage of those

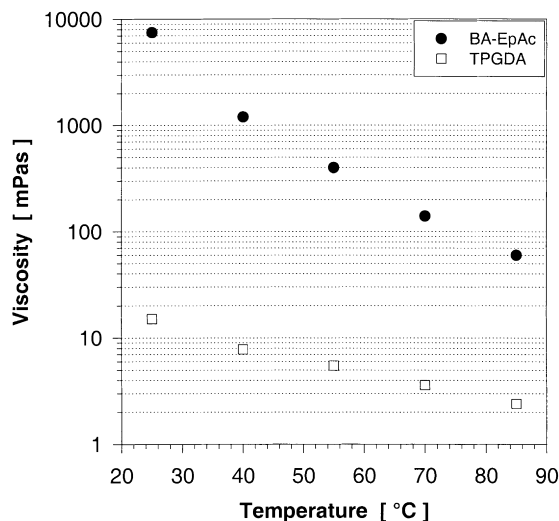


Fig. 7. Viscosity of BA-EpAc and TPGDA.

radicals is needed to consume the oxygen dissolved in the sample. However, at temperatures higher than 70°C a reverse dependence of the induction period on the temperature is observed. This does not indicate a re-increase of the oxygen solubility in the acrylate but a reduced ability of the system to overcome inhibition. Obviously, the radical concentration in the initial phase of the photoinduced reaction seems to decrease with the increasing temperature. However, the recombination of primary radicals is known to be negligible [37].

A remarkable feature is the close coincidence between the temperature dependence of $R_{p,\max}$ and t_i where both show a reversal of their behaviour in the same temperature region. The proposed decrease of the radical concentration would also explain the drop of $R_{p,\max}$ at higher temperatures. This is discussed in more detail below.

Samples containing BDMB as photoinitiator do not show

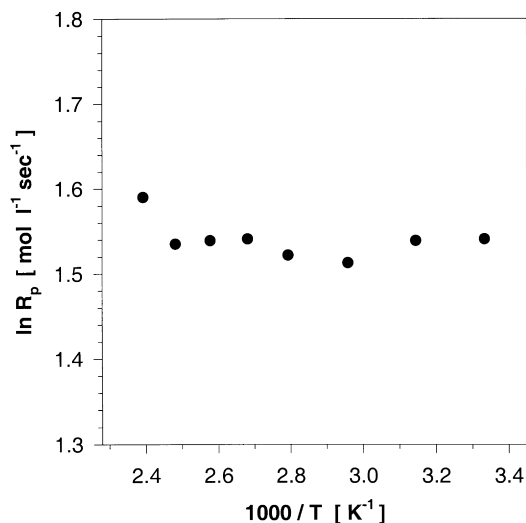


Fig. 8. Arrhenius plot of TPGDA/0.1 wt.% BDMB (irradiance 58 mW cm^{-2}).

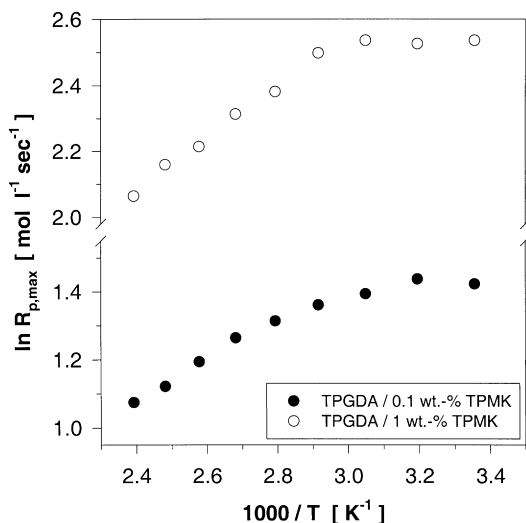


Fig. 9. Arrhenius plot of TPGDA with 0.1 or 1 wt.% TPMK (irradiance 56 mW cm^{-2}).

an induction period detectable within the temporal frame of the RTIR method.

3.3.2. Initiation with BDK and HAP

Besides the two morpholino ketones, two other photoinitiators were tested in respect of their influence on the temperature dependence of the kinetics of photopolymerization of TPGDA. Both the α -hydroxy alkylphenone (HAP) and benzildimethyl ketal (BDK) have much lower extinction coefficients at 313 nm than the morpholino ketones studied before. They were added to TPGDA with 1 wt.%. Their effect on the temperature dependence of the maximum polymerization rate is shown in Fig. 11.

Both the Arrhenius plots are quite different from those of the morpholino ketones. The two curves show the usual Arrhenius-like behaviour, i.e. $R_{p,max}$ increases with tempera-

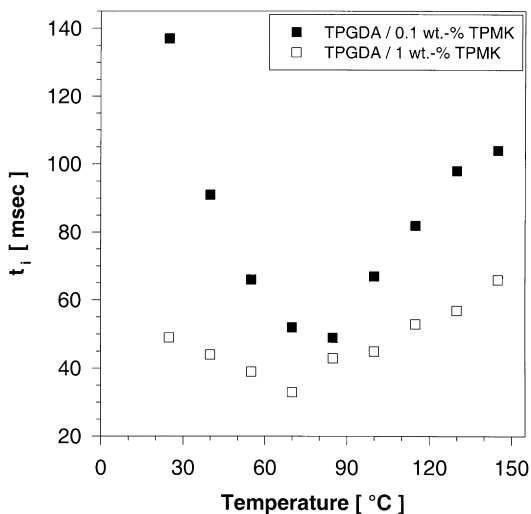


Fig. 10. Temperature dependence of the induction period of TPGDA with 0.1 or 1 wt.% TPMK (irradiance 56 mW cm^{-2}).

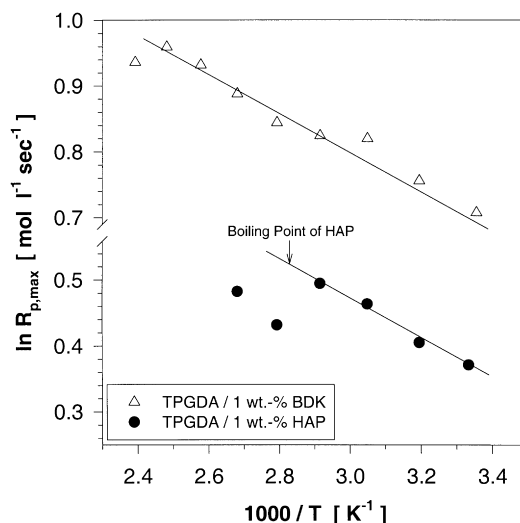


Fig. 11. Arrhenius plot of TPGDA with 1 wt.% BDK or HAP, respectively (irradiance 60 mW cm^{-2}).

ture throughout the whole temperature range studied, and no drop of the polymerization rate at higher temperatures is observed. The scatter of the data of HAP at 85 and 100°C is due to the beginning evaporation of this initiator at 80°C .

The apparent activation energy of the polymerization reaction calculated from the slope of the two plots was found to be 2.3 kJ mol^{-1} with BDK and 2.5 kJ mol^{-1} with HAP. This is in the same range like a value reported for hexanediol diacrylate (3.7 kJ mol^{-1}) [1] yet about one order of magnitude less than the activation energy of the epoxy diacrylate. As expected, this is consistent with the lower drop of the viscosity of TPGDA in this temperature region (see Fig. 7).

Increasing the temperature also leads to a rise of the final conversion of TPGDA (Fig. 12) since more residual double bonds become accessible for polymerization due to the enhancement of the segmental mobility in the network.

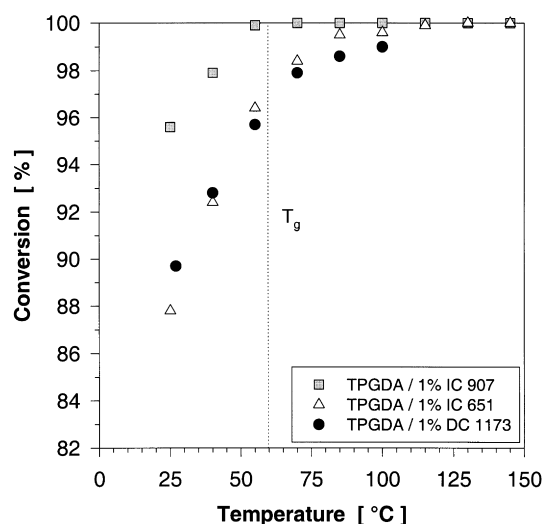


Fig. 12. Conversion of TPGDA/1 wt.% photoinitiator after 10 s irradiation.

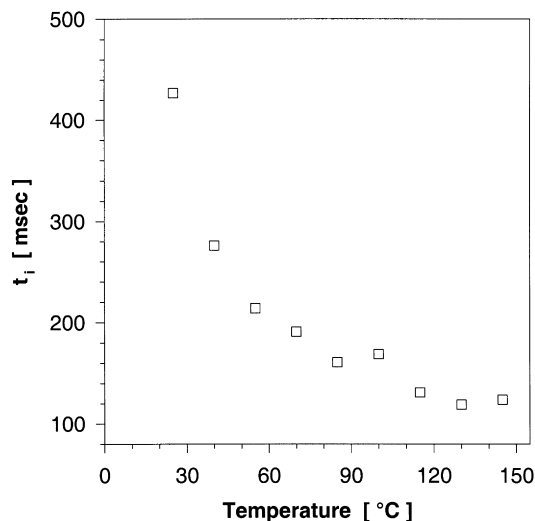


Fig. 13. Temperature dependence of the induction period of TPGDA/1 wt.% BDK (irradiance 60 mW cm^{-2}).

Using TPMK, complete cure is already achieved at 55°C , whereas a steady increase of the conversion of double bonds up to temperatures higher than 100°C is observed on initiation with HAP and BDK.

The influence of temperature on the induction period of TPGDA with BDK or HAP is plotted in Figs. 13 and 14. Using these two initiators, the induction period at room temperature is much longer than with the morpholino ketones. With increasing temperature, a strong decay of t_i is observed. However, in contrast to the temperature behaviour with morpholino ketones, the decay proceeds continuously throughout the whole range of temperatures. This clearly reflects the continuous increase of $R_{p,\max}$ for BDK and HAP. Again coinciding temperature behaviour of $R_{p,\max}$ and t_i is observed as was already found for TPMK.

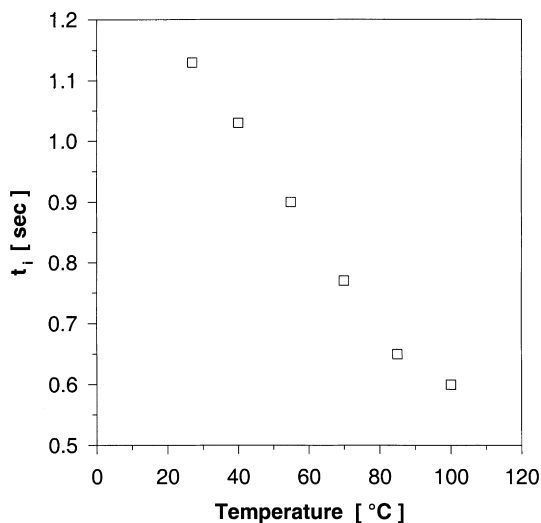


Fig. 14. Temperature dependence of the induction period of TPGDA/1 wt.% HAP (irradiance 60 mW cm^{-2}).

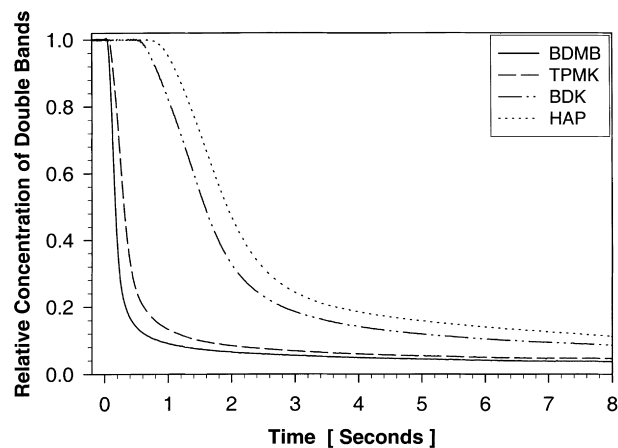


Fig. 15. Photopolymerization of TPGDA with various photoinitiators (concentration 1 wt.%) on irradiation with 313 nm.

3.3.3. Effect of photoinitiator on the temperature dependence of the photopolymerization

It is obvious from Figs. 4 and 9–14 that there are two groups of photoinitiators which lead to quite different temperature dependence of the photopolymerization of acrylates. The first group which consists of BDK and HAP shows the usual Arrhenius behaviour of $R_{p,\max}$ and a continuous decrease of t_i . In contrast, initiation with morpholino ketones leads to a singularity in the temperature dependence of the polymerization with a reversal of the behaviour of $R_{p,\max}$ and t_i .

The different behaviour of the two groups of photoinitiators is supposed to be due to the considerable differences of their absorption coefficients at 313 nm (see Table 1) which differ by two orders of magnitude or even more. This leads to huge differences for the numbers of radicals generated on irradiation and thus to different efficiencies in starting the photopolymerization reaction (Fig. 15).

At lower temperatures, propagation is dominating. With increasing temperature, the autoacceleration effect diminishes due to the mobilization of free radical chain ends and termination becomes more prominent which affects the polymerization rate. The fact that $R_{p,\max}$ was found to be proportional to $I_0^{0.5}$ [24,38] indicates that largely bimolecular termination processes occur. The probability of radical recombination and disproportionation reactions is proportional to the square of the radical concentration which should cause a strong effect of the number of radicals on the decay of $R_{p,\max}$. The high absorption coefficients of the morpholino ketones lead to much higher radical concentrations than for the other two photoinitiators. The resulting stronger extent of termination processes leads to a decrease of $R_{p,\max}$ with these two photoinitiators when the temperature increases.

Moreover, chain transfer occurs which is energetically favoured by elevated temperatures and also by a high concentration of small initiator molecules [4]. Chain transfer can play an important role for termination since it

maintains a certain mobility of radicals in the network that would be otherwise rather limited. The transport of radicals results in an increase of recombination reactions. This way, chain transfer leads to a drop of the rate of polymerization [2,5,17]. At temperatures higher than 90°C, termination and chain transfer more and more dominate the polymerization, which is reflected in a marked decrease of the maximum polymerization rate with increasing temperature.

At this stage of the discussion, the reasons for the different temperature behaviour of the two groups of photoinitiators, in particular with respect to the induction period, are not yet completely understood. Further studies on this subject are in progress in order to obtain a deeper insight into those phenomena.

3.4. Thermal Side Effects

If photopolymerization is performed at higher temperatures, it has to be taken into account that thermal side effects such as evaporation of the reactants, thermal degradation of monomer, photoinitiator, or polymer, or thermal initiation of the polymerization might occur which could influence the curing reaction and its kinetics. The occurrence of such effects has been discussed in previous investigations by photo-DSC on the photopolymerization of dimethacrylate oligomers [11,15].

In order to estimate the extent of such side reactions, some investigations were performed by DSC, thermogravimetry, and gas chromatography with head space attachment.

TPGDA and the epoxy diacrylate were heated in the DSC with 10°C min⁻¹ from room temperature to 300°C. In both acrylates, a strong exothermic peak was observed at about 205°C, i.e. thermal polymerization just starts at a temperature which is well above the temperature range investigated in the present study.

Moreover, TPGDA was heated in the DSC to 80, 100, 120, and 150°C, respectively, and kept at these temperatures for 60 min. At none of these temperatures any heat flow indicating the occurrence of thermal polymerization or degradation was observed. When TPGDA was heated in the TGA to 100°C and then held under isothermal conditions for further 10 min, a total weight loss of 3.8% was found. The volatiles were identified by GC headspace as tripropylene glycol and its monoacrylated derivative, i.e. as impurities from synthesis rather than as degradation products.

The thermal stability of the photoinitiators was tested by DSC and TGA. No indication for decomposition or evaporation up to 200°C was found. The only exception is HAP which starts to evaporate at 80°C. A total weight loss of 28 wt.% after 30 min at 80°C and 45 wt.% at 100°C, respectively, was observed for this initiator.

The total contact time of the acrylate with the heated ATR crystal for achieving the temperature equilibrium usually was less than 8 min, i.e. it was shorter or as long as during thermal studies. During this time, the sample is covered by

the quartz plate, which largely prevents the loss of the material.

From all these findings it can be concluded that thermal side effects have at most a minor contribution to the total effect of temperature on photopolymerization on the time scale of our experiments.

Another aspect which has to be considered is the rise of temperature during irradiation due to the release of the polymerization heat. Under adiabatic conditions, it would surpass the effect of external heating by far and thus completely mask it, in particular when highly reactive multifunctional monomers are used [32,39]. However, the diamond and the tungsten carbide disc into which it is bound ensure good thermal contact between sample and ATR unit enabling an effective heat transfer. The actual temperature increase due to the reaction enthalpy was estimated with thermo-responsive foils (resolution of 5°C) which were in contact with the sample during irradiation. The maximum rise of temperature was found to be less than 10°C. Thus, the photopolymerization reaction proceeds under nearly isothermal conditions.

4. Conclusions

The effect of temperature on the kinetics of the photopolymerizations of a highly viscous epoxy diacrylate and TPGDA as system of lower viscosity was studied by real-time FTIR-ATR spectroscopy. In the more viscous system, the polymerization rate was found to strongly increase with temperature up to 90°C. The apparent activation energy was determined to be 13.5 kJ mol⁻¹. It was shown by the investigation of mixtures from BA-EpAc and TPGDA that the increase of R_p is largely due to the dramatic drop of viscosity in this temperature region. At temperatures higher than 90°C, the polymerization rate decreases with increasing temperature.

In TPGDA, the temperature dependence of the polymerization kinetics shows a marked influence of the photoinitiator used for initiation. Using benzildimethyl ketal or the α -hydroxy alkylphenone, the usual Arrhenius behaviour with a slight increase of the polymerization rate within the whole temperature region under investigation was observed (apparent activation energy ca. 2.4 kJ mol⁻¹). Simultaneously, the induction period was found to decrease continuously due to the decreasing solubility of oxygen in the acrylate.

In contrast, initiation with morpholino ketones leads to a substantial change of the temperature dependence of the kinetics at about 70 to 90°C. At lower temperatures, $R_{p,max}$ was found to be independent of temperature followed by a distinct decay above 90°C. The induction period first diminishes with temperature. When $R_{p,max}$ starts to decrease, a re-increase of t_i is observed.

The different kinetic behaviour is assumed to be due to large differences between the absorption coefficients of the

photoinitiators and consequently the number of radicals generated on irradiation. The higher radical concentration in systems containing morpholino ketones should lead to a more important role of termination processes when temperature rises. Moreover, chain transfer is favoured at elevated temperatures. Both processes affect the polymerization rate in the temperature region above 90°C.

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